

# Absence of molybdenum isotope fractionation during magmatic differentiation at Hekla volcano, Iceland

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## Abstract

This study investigates the behaviour of molybdenum (Mo) isotopes during magmatic differentiation. Molybdenum isotope compositions, as well as concentrations of rare earth elements and a selection of trace elements, have been determined for a well characterised sequence of lavas from Hekla volcano, Iceland, covering a compositional range from basalt to rhyolite (46–72 wt.% SiO<sub>2</sub>), and thought to have developed by differentiation and mixing of melts derived from a cogenetic source. All samples have identical Mo isotopic compositions with an average  $\delta^{98}\text{Mo}$  of  $-0.15 \pm 0.05\%$  (2 s.d.;  $n = 23$ ). There is therefore no resolvable Mo isotope fractionation during magmatic differentiation at Hekla. This finding is supported by the fact that Mo remains highly incompatible in Hekla lavas, increasing from 1.3 to 4.6  $\mu\text{g/g}$  from basalt to rhyolite, indicating that the crystallising phases are extracting only limited amounts of Mo from the magma and therefore that significant fractionation of Mo isotopes is unlikely. It has previously been proposed that cerium (Ce) and Mo have similar bulk distribution coefficients and are equally incompatible during mantle melting. While both Ce and Mo remain incompatible in Hekla lavas, the Ce/Mo ratio decreases from 50 to 36 during magmatic differentiation indicating that Mo is more incompatible than Ce. Comparison of Mo with other incompatible trace elements indicates that Mo is as incompatible as La and slightly less incompatible than K. Sulphur (S) decreases strongly from  $\sim 200$  to as low as  $\sim 2 \mu\text{g/g}$  from basalt to andesite and more evolved compositions, yet this has no effect on the Mo isotopes. Therefore, Mo does not exhibit significant chalcophile behaviour in Hekla magmas. The Mo isotopic signature therefore may be used as an indicator of parent magma composition and a potential discriminant of assimilation processes.

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## 1. INTRODUCTION

As a redox sensitive element with seven stable isotopes, molybdenum (Mo) holds great potential for deciphering the geological past. Molybdenum isotope data coupled with Mo concentrations have been used to reconstruct the

history of the redox state of the oceans (e.g. Siebert et al., 2003; Anbar, 2004; Pearce et al., 2008; Gordon et al., 2009). It has become clear that Mo isotope fractionation can occur at low-temperatures during redox reactions (e.g. Tossell, 2005; Nägler et al., 2011), Mn–Fe oxides absorption (e.g. Barling and Anbar, 2004; Wasylenki et al., 2008), and biological utilisation (e.g. Zerkle et al., 2011).

The distinctive Mo isotope compositions characteristic of different low-T settings, make Mo attractive as a tracer

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of crust–mantle recycling processes. However, our knowledge of high-T effects on Mo isotopes is limited. Data exist only for a limited number of igneous rocks (Siebert et al., 2003; Voegelin et al., 2012, 2014), and high-T (300–600 °C) hydrothermal ore deposits (Hannah et al., 2007; Mathur et al., 2010; Greber et al., 2011, 2014).

Relatively large ranges in  $\delta^{98}\text{Mo}$  of 1.8‰ (Wieser and De Laeter, 2003), 1.9‰ (Hannah et al., 2007), 2.4‰ (Mathur et al., 2010), 1.4‰ (Greber et al., 2011) and 0.88‰ (Greber et al., 2014), have been found in high-T molybdenites from a variety of ore deposits. Hannah et al. (2007) ascribe the variations they observed to Rayleigh distillation during the precipitation of molybdenite from a propagating molybdate-bearing vapour phase. However, a bimodal distribution of Mo isotope compositions has been reported for molybdenites from the Swiss Alps, which favours redox variation as the major controlling factor (Greber et al., 2011).

The occurrence of molybdenite covers a wide temperature range, from 50 to 600 °C in hydrothermal deposits. It can also be produced at  $\geq 700$  °C as an accessory igneous mineral (Wieser and DeLaeter, 2007). Apart from forming molybdenite or occasionally molybdate, it has in the past been thought that Mo will be incorporated into  $\text{Fe}^{3+}$ - and  $\text{Ti}^{4+}$ -rich minerals, such as pyroxene, ilmenite, magnetite or sphene, as a result of substitution (Wager and Mitchell, 1951; Annersten and Ekström, 1971). So far it has not been ascertained what if any effect magmatic evolution and the crystallisation of Mo-bearing minerals has on Mo isotopes.

Data for igneous rocks are more limited. Siebert et al. (2003) found a narrow fractionation range in six Kamchatka basalts, and two Himalaya granites, with average  $\delta^{98}\text{Mo} \sim -0.15$ ‰ and concluded that magmatic processes play a minor role in Mo isotope fractionation. The isotopic input of the continental crust to the ocean has since been thought to be approximately zero (e.g. Duan et al., 2010; Pearce et al., 2010). However, recent analyses of the Mo isotope composition in riverine waters have shown a broad range of variation (Archer and Vance, 2008; Pearce et al., 2010; Neubert et al., 2011; Voegelin et al., 2012). A recent study on Mo isotopes in a magmatic system found differences of up to 0.3‰ between basalts and rhyolitic pumice from Kos Plateau Tuff, Aegean Arc, which the authors attributed to magmatic differentiation (Voegelin et al., 2014). Here we systematically address magmatic differentiation using the example of the lavas from Hekla volcano Iceland that have erupted through a section of crust with no deep crustal sedimentary rocks (see Savage et al., 2011).

## 2. GEOLOGIC BACKGROUND

Iceland straddles the Mid-Atlantic Ridge, and formed in response to the upwelling of the Icelandic plume and the opening of the Atlantic Ocean. Most of the island is covered by young extrusives, with the oldest rock being approximately 13 Ma (Moorbath et al., 1968). Compared to lavas erupted in continental settings, Icelandic magmas are much less likely to undergo contamination by metasediment. As such they are ideal for studying the isotopic

effects of crystal fractionation in the absence of such complications.

Hekla volcano, located in the South Iceland Volcanic Zone, is one of many active volcanoes on Iceland. There have been 18 eruptions since 1104 A.D., and 5 prehistoric eruptions have been identified (Sigmarsson et al., 1992; Höskuldsson et al., 2007, and references therein). Hekla is known for its wide spectrum of cogenetically sourced volcanic products, covering basalt, andesite, dacite and rhyolite, developed from differentiation in the magma chamber (Thordarson and Larsen, 2007; Savage et al., 2011). It is an active fissure volcano with no associated caldera or geothermal activity (Sigmarsson et al., 1992; Soosalu and Einarsson, 2004). Therefore, the successively evolved magmatic differentiates are ideal for studying the response of Mo isotopes to magmatic differentiation.

The differentiation of Hekla magmas has been investigated in detail. Hekla lavas of basaltic to silicic composition are seen to have similar and mantle-like radiogenic Sr–Nd isotopes, which suggest the same or similar source origin for Hekla series (Sigmarsson et al., 1992; Chekol et al., 2011). Although simple fractional crystallisation in a closed system from basaltic to silicic melts is favoured from the perspective of  $\text{H}_2\text{O}/\text{K}_2\text{O}$  (Portnyagin et al., 2012), involvement of pre-existing Icelandic lower crust for the production of andesite to rhyolite has also been suggested by other models (e.g. Sigmarsson et al., 1992; Schuessler et al., 2009; Chekol et al., 2011). Based on  $^{238}\text{U}$ – $^{230}\text{Th}$  data, Sigmarsson et al. (1992) proposed the following three-stages to generate the magma series in a compositionally zoned magma chamber: (1) basaltic magmas rise and trigger partial melting of the lower part of metabasaltic Icelandic crust, generating dacitic magma; (2) the basaltic magma and dacitic magma evolve by crystal fractionation to produce basaltic andesite and rhyolitic magma, respectively; (3) mixing of basaltic andesite and dacitic melts produces andesites. Nevertheless, a study on  $^{238}\text{U}$ – $^{230}\text{Th}$ – $^{226}\text{Ra}$  disequilibria for Hekla magmas suggested that the basaltic andesites were derived from basalt by fractional crystallisation and the more evolved magmas of andesitic to silicic composition were derived from AFC (assimilation and fractional crystallisation; DePaolo (1981)) processes (Chekol et al., 2011). The disagreement over the origin of the andesitic to silicic magma is not a concern for this study, as long as magmatic differentiation and/or remelting of cognate material link the production of the entire sequence of Hekla lavas.

Hydrothermal alteration at Hekla has been inferred to be insignificant on the basis of lines of evidence, such as Sr and O isotopes. Seawater, geothermal fluids and rocks that have been hydrothermally altered by seawater have much higher  $^{87}\text{Sr}/^{86}\text{Sr}$  than pristine mantle rocks (Elderfield and Greaves, 1981). The mantle-like values of radiogenic Sr and Nd isotopes for the entire compositional range of Hekla lavas (Sigmarsson et al., 1992) are inconsistent with large scale contamination of the source by such material. In addition, hydrothermal alteration can result in considerably lower  $\delta^{18}\text{O}$  in affected materials (e.g. Hemond et al., 1993; Hattori and Muehlenbachs, 1982). Hekla lavas, like other Icelandic lavas, have lighter stable

oxygen isotope compositions ( $4.5‰ \leq \delta^{18}\text{O} \leq 5.3‰$ ) than normal mantle values ( $\delta^{18}\text{O} = 5.5‰$ ) (Sigmarsson et al., 1992; Matthey et al., 1994), which could imply contamination introduced from a hydrothermally altered source. However, the low- $\delta^{18}\text{O}$  has been proposed to originate from deep in the mantle and to be a common feature of extrusives on Iceland due to the lack of other geochemical evidence suggestive of an altered component in many pristine samples (Thirlwall et al., 2006).

The effect of magmatic differentiation on lithium (Li), silicon (Si), zinc (Zn), vanadium (V) and iron (Fe) isotope systems has been systematically investigated for Hekla lavas. Resolvable isotope fractionation interpreted to result from magmatic differentiation has been observed for Fe, V, and Si. There is an increase of  $0.117 \pm 0.021‰$  in  $\delta^{56/54}\text{Fe}$  from dacite to rhyolite, but no fractionation was detected in the basaltic system (Schuessler et al., 2009). A large range in  $\delta^{51}\text{V}$  ( $\sim 2‰$ ) was found in basaltic and basaltic andesite lavas, thought to be related to the incorporation of light V isotopes into magnetite (Prytulak et al., 2012). Savage et al. (2011) found a systematic Si isotopic fractionation as a result of magmatic differentiation through the entire sequence of Hekla magmas (see Fig. 5a in Savage et al., 2011). Lithium isotopes do not vary with magmatic differentiation on Hekla (Schuessler et al., 2009). Similarly, although Zn isotopic fractionation has been found as a function of magmatic indices elsewhere, systematic fractionation in Hekla lavas was not observed (Chen et al., 2013).

### 3. SAMPLES AND METHODS

Twenty-three samples from Hekla volcano, covering basalt, basaltic andesite, andesite, dacite and rhyolite, as well as two unrelated Icelandic samples were analysed for  $\delta^{98}\text{Mo}$ , and Mo and rare earth elements (REE) concentrations. A sketch map with localities of samples collected for this study is provided in Savage et al. (2011). The  $\text{SiO}_2$  content of these samples ranges from 46 to 72 wt.%, spanning the range of previously studied Hekla rocks (Sigmarsson et al., 1992; Schuessler et al., 2009). The same samples were previously studied for Si isotopes, major and a selection of trace elements by Savage et al. (2011). Two USGS standards, BHVO-2, GSP-2, were analysed as additional samples to provide a long-term monitor of analytical reproducibility. All samples were crushed to powder in an agate mill at the Open University, Milton Keynes (Savage et al., 2011). Aliquots for Mo isotope ratio and concentration analysis were weighed in the amount of  $\sim 100$  mg for each sample, and then double spiked with a known quantity of a  $^{97}\text{Mo}$  and  $^{100}\text{Mo}$  isotope tracer in order to correct for experimental and instrumental Mo isotope fractionation (Siebert et al., 2001). Samples were then dissolved in Savillex PFA vials by successive acid digestions using  $\text{HF-HNO}_3$ ,  $\text{HNO}_3$ , and  $\text{HCl}$  on hotplate at  $90\text{--}120^\circ\text{C}$ . The aliquots for Mo isotope analysis were processed through three steps of column chemistry using anion (Biorad AG1-X8) and cation resin (AG50W-X8) to guarantee effective separation of Mo from the matrix, following the method of Mo purification described by Wasylenki et al. (2007). The high Fe/Mo ratio

in igneous rocks and the potential isobaric interference of  $^{56}\text{Fe}^{40}\text{Ar}$  on  $^{96}\text{Mo}$ , require two modifications that were made in this study for better separation of Mo from Fe: (1) the cation resin separation was processed twice using new resin each time; (2)  $30\ \mu\text{l} \sim 30\%$   $\text{H}_2\text{O}_2$  was added to sample solutions before loading onto the cation resin column. Isotope compositions were measured by a Nu Instruments multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) in low resolution at the University of Oxford, following the method of Siebert et al. (2001). Molybdenum isotope measurements were made relative to an Alfa Aesar ICP standard solution (Lot 011895D). As NIST SRM3134 has been agreed upon as an international Mo standard (Greber et al., 2012; Goldberg et al., 2013), our Mo isotope composition data are normalised to NIST SRM3134, where the  $\delta^{98}\text{Mo}$  of NIST SRM3134 is set to  $0‰$ , in order to facilitate inter-laboratory comparison. Data are reported in  $\delta^{98}\text{Mo}$  notation expressed as

$$\delta^{98}\text{Mo} = \left[ \frac{(^{98}\text{Mo}/^{95}\text{Mo})_{\text{sample}}}{(^{98}\text{Mo}/^{95}\text{Mo})_{\text{standard}}} - 1 \right] \times 1000$$

The Oxford Alfa Aesar standard solution used in this study has a  $\delta^{98}\text{Mo}$  value of  $-0.12 \pm 0.06‰$  relative to NIST SRM3134 (Greber et al., 2012). In addition, all Mo isotope compositions cited from the literature in this study have been renormalised to NIST SRM3134, using the values recommended by Goldberg et al. (2013). Full procedural duplicates of the USGS rock standards BHVO-2 ( $n = 10$ ) and GSP-2 ( $n = 15$ ), give an external reproducibility of  $0.06‰$  (2 s.d.), and yield Mo isotope compositions of  $0.01 \pm 0.06‰$  and  $-0.17 \pm 0.06‰$ , respectively, relative to NIST SRM3134. The Mo isotope composition of BHVO-2 measured in this study ( $\delta^{98}\text{Mo} = 0.01 \pm 0.06‰$  (2 s.d.)) is identical within uncertainty to the values of  $\delta^{98}\text{Mo} = -0.06 \pm 0.14‰$  (2 s.d.) and  $-0.05 \pm 0.12‰$  (2 s.d.) determined by Burkhardt et al. (2014) and Li et al. (2014), respectively. A minimum of two full procedural duplicates was made for each sample analysed. Reproducibility (2 s.d.) of all samples is better than  $0.06‰$ .

The concentrations of Mo were determined by isotope dilution MC-ICP-MS using the double spike isotopic composition data. The long-term average Mo concentrations of USGS standards are: BHVO-2 =  $3.5 \pm 0.9\ \mu\text{g/g}$  (2 s.d.,  $n = 10$ ) and GSP-2 =  $2.1 \pm 0.4\ \mu\text{g/g}$  (2 s.d.,  $n = 15$ ). The Mo concentrations of GSP-2 analysed in this study show excellent consistency for 15 digestions and the average concentration of  $2.1 \pm 0.4\ \mu\text{g/g}$  is in agreement with the USGS recommended value,  $2.1 \pm 0.6\ \mu\text{g/g}$ . The relatively high 2 standard deviation of  $\pm 0.9\ \mu\text{g/g}$  for 10 digestions of BHVO-2 reflects substantial heterogeneity in terms of Mo concentration. The inconsistency of Mo contents of BHVO-2 has also been reported by previous studies with [Mo] ranging from 2.8 to  $5.5\ \mu\text{g/g}$  (Li et al., 2014; Burkhardt et al., 2014). Also Mo abundances in BHVO-1 and BHVO-2, which are from the same Kilauea lava flow, have been shown to differ by a factor of four (Weis et al., 2005). Such heterogeneity was therefore suggested to be the result of Mo contamination during sample preparation (Weis et al., 2005; Burkhardt et al., 2014). Hence, caution is

needed in using BHVO-2 or BHVO-1 for inter-lab comparisons of Mo concentration and isotopic composition.

Sample and USGS standard aliquots for REE and trace element analysis were dissolved separately using HF, HNO<sub>3</sub>, and HCl digestions in Savillex® PFA vials. The concentrations of REEs were determined using a Thermo-Finnigan Element 2 HR-ICP-MS in wet plasma mode, using a quartz cyclonic spray chamber with a self-aspirating 100 µl/min uptake PFA nebulizer. Conventional techniques (e.g. Jenner et al., 1990), employing internal standards, standard additions and external standards were used for analysis. Calibration was achieved by the method of standard additions in order to overcome any matrix effect. This involved spiking two samples with a REE standard solution at five different concentrations. A basalt and a dacite were chosen for this, and the calibration curves derived were then used to calculate REE concentrations for basalts to basaltic andesites and andesites to rhyolites, respectively. Internal standards, Rh and Re for LREE and HREE respectively, were doped in samples to correct for instrumental drift. Gravimetrically prepared multi-element monitor standard solutions were measured every 5 samples to determine precision and accuracy. The average relative standard deviation (RSD) and accuracy (defined as the absolute value of  $(1 - ([\text{El}] \text{ measured value } / [\text{El}] \text{ certified value}))\%$ ) are 1.8% and 1.7%, respectively for REEs and trace elements in the monitor standards. The average accuracy of BHVO-2 and GSP-2, is 3.5% and 6.8%, respectively, relative to USGS recommended values. Individual element RSD and accuracy are listed in the [Electronic annex](#).

#### 4. RESULTS

All data are presented in [Table 1](#) and the [Electronic annex](#). The average Mo concentrations in Hekla samples are 1.4 µg/g, 2.6 µg/g, 2.9 µg/g, 3.9 µg/g, and 4.6 µg/g, for basalts, basaltic andesites, andesites, dacites, and rhyolites respectively. These values are higher than the Mo concentration of 1.1 µg/g estimated for average continental crust (Rudnick and Gao, 2003). In contrast to the Fe (Schuessler et al., 2009) and Si (Savage et al., 2011) isotope systems, Mo isotope compositions for the 23 Hekla samples are strikingly uniform: average  $\delta^{98}\text{Mo} = -0.15 \pm 0.05\%$  (2 s.d.,  $n = 23$ ) and display no correlation with Mo concentration or silica content ([Fig. 1a](#) and [b](#)). The two additional samples BUR20-09 and rhyolite RHY01-09, which are unrelated to Hekla, have Mo isotope compositions of  $-0.07 \pm 0.06\%$  and  $-0.06 \pm 0.06\%$ , within error of the value for the Hekla lavas ([Table 1](#)).

#### 5. DISCUSSION

##### 5.1. Behaviour of molybdenum during fractional crystallisation

The behaviour of Mo during magmatic differentiation at Hekla is illustrated in [Fig. 2](#). It can be seen that Mo concentrations in the Hekla volcanic rocks are correlated with magmatic differentiation indicators (SiO<sub>2</sub>, K). Molybdenum has

been inferred to have a bulk solid/liquid distribution coefficient ( $D$ ) similar to that of the light to middle rare earth elements, Ce, Nd, and Pr, based on the constancy of the Mo/Ce, Mo/Nd, Mo/Pr ratios observed in various terrestrial samples (Sims et al., 1990; Newsom and Palme, 1984; Newsom et al., 1986). Hekla lavas show that although statistically indistinguishable, the Ce/Mo ratio decreases systematically from 50 to 36 from basalts to rhyolites, indicating that Mo is slightly more incompatible than Ce during magmatic differentiation ([Fig. 3a](#)). Both elements remain incompatible (bulk  $D < 1$ ) throughout the sequence however. In contrast to the relative incompatibility expected for mantle melting (Sun and McDonough, 1989), Mo is more incompatible than Nb and Ta during magmatic differentiation at Hekla ([Fig. 3c](#) and [d](#)), with a decrease from 29 to 17 for Nb/Mo and 1.7 to 0.4 for Ta/Mo. This presumably reflects the removal of accessory phases that fractionate high field strength elements (HFSE). Rubidium is more incompatible than Mo, the Rb/Mo nearly doubling from 8 to 14 from basalt to rhyolite ([Fig. 3e](#)). The K/Rb displays a concomitant decrease from 430 to 350. As a result, the K/Mo ratio increases only slightly from  $\sim 4,000$  to  $\sim 5,000$  ([Fig. 3f](#)). Therefore, the bulk  $D$  for Mo these in magmas must lie between that of K and that of Ce. This is confirmed by inspection of the La/Mo ratio, which is relatively uniform in Hekla lavas ([Fig. 3b](#)). There seems to be a hint of differences in La/Mo and Ce/Mo ratios between basalt and dacite ([Fig. 3a](#) and [b](#)), and the ratios of andesite fall in between them, which could be an indication of mixing effect. This concurs with the proposed three-stages model for Hekla magmas (Sigmarsson et al., 1992). The difference between basalt and dacite in La/Mo or Ce/Mo may have resulted from processes related to partial melting. While this is consistent with the three-stage model, it should be noted that the effect is small; the LREE/Mo ratios for all Hekla lavas are very similar.

Given the number of samples studied it can be stated with some confidence that the Mo isotope composition of Hekla volcanic rocks is uniform within error, with an average  $\delta^{98}\text{Mo}$  of  $-0.15 \pm 0.05\%$  (2 s.d.) ([Fig. 1](#)). Interestingly, Icelandic samples from other localities unrelated to Hekla volcano, including two samples (BUR20-09 and RHY01-09) analysed in this study and a few basalts from Iceland in Liang (2013), have Mo isotope compositions similar to Hekla lavas. Therefore, this composition of  $\delta^{98}\text{Mo} \sim -0.1\%$  appears likely to be representative of basaltic magmas and their differentiates from the Icelandic plume and represent a common feature of much of the Iceland crust.

This lack of variation in Mo isotope composition in Icelandic lavas is in marked contrast to the positive linear correlation found for these samples between Si isotopes and SiO<sub>2</sub> content, interpreted to be caused by Si isotope fractionation during magmatic differentiation (Savage et al., 2011). Therefore, crustal magmatic differentiation in this deliberately chosen “simple” system does not change Mo isotopes at currently resolvable levels. Of course, some other magmatic systems may be more complex than Hekla.



Table 1

Mo isotope and a selection of trace elements data for Hekla lavas.

Sample	Rock Type	Age	Mo μg/g	$\delta^{98}\text{Mo}$ ‰	SiO <sub>2</sub> wt. %	$\delta^{30}\text{Si}$ ‰	K μg/g	Rb μg/g	S μg/g	La μg/g	Ce μg/g	Nb μg/g	Ta μg/g
<i>Hekla lavas</i>													
HEK04-09	Basalt	1878 A.D.	1.4	−0.18	46.97	−0.31	5399	12.1	123.4	26.7	62.3	39.2	2.4
HEK05-09	Basalt	1913 A.D.	1.3	−0.18	46.47	−0.32	5218	12.2	150.7	28.1	66.7	37.7	2.1
HEK06-09	Basalt	1913 A.D.	1.3	−0.16	46.20	−0.31	5284	11.8	172.2	26.2	62.1	39.0	2.1
HEK07-09	Basalt	1878 A.D.	1.4	−0.11	46.64	−0.34	5307	12.7	123.7	26.2	60.5	38.5	1.8
HEK09-09	Basalt	1878 A.D.	1.5	−0.15	47.01	−0.28	5742	12.3	122.2	28.3	66.2	40.8	2.1
HEK12-09	Basalt	1913 A.D.	1.4	−0.12	46.42	−0.29	5592	13.5	104.1	27.4	66.0	41.0	2.3
HEK02-09	Basaltic andesite	1970 A.D.	2.6	−0.13	53.92	−0.25	10357	24.8	31.2	50.4	115.8	58.5	3.2
HEK03-09	Basaltic andesite	1970 A.D.	2.6	−0.17	54.05	−0.22	10,389	24.9	39.5	49.4	113.5	59.4	3.1
HEK08-09	Basaltic andesite	1970 A.D.	2.7	−0.18	54.59	−0.29	11,046	27.0	49.0	52.0	117.3	59.6	3.3
HEK13-09	Basaltic andesite	1991 A.D.	2.5	−0.16	53.90	−0.29	10,182	23.8	56.8	49.9	117.4	57.0	2.9
HEK14-09	Basaltic andesite	1991 A.D.	2.4	−0.15	53.71	−0.26	10,246	24.9	39.2	50.0	114.8	57.2	3.1
HEK16-09	Basaltic andesite	1980 A.D.	2.6	−0.15	54.81	−0.27	10,634	25.7	42.1	50.6	114.8	59.6	3.0
HEK17-09	Basaltic andesite	1980 A.D.	2.6	−0.11	54.57	−0.25	10,494	25.5	57.7	49.9	116.0	57.0	2.8
HEK21-09	Basaltic andesite	1390 A.D.	2.7	−0.17	55.64	−0.29	11,162	28.6	25.7	51.9	117.7	59.5	2.8
HEK10-09	Andesite	1947 A.D.	2.8	−0.15	57.67	−0.25	12,238	31.2	14.6	50.9	115.3	56.2	2.6
HEK11-09	Andesite	1947 A.D.	2.7	−0.18	58.09	−0.23	12,187	31.2	5.8	50.7	115.4	58.2	2.3
HEK15-09	Andesite	1980 A.D.	3.2	−0.12	59.64	−0.22	13,754	35.0	13.8	57.6	130.1	69.7	2.4
HEK01-09	Dacite	2800 B.P.	3.9	−0.14	68.71	−0.18	19,202	54.1	0.0	67.2	147.6	66.5	1.9
HEK02-10	Dacite	2800 B.P.	3.9	−0.10	68.31	−0.21	19,025	51.9	37.5	67.2	145.4	66.9	3.1
HEK18-09	Dacite	2800 B.P.	3.9	−0.12	68.41	−0.17	19,130	53.2	2.2	66.7	145.1	65.8	2.9
HEK19-09	Dacite	2800 B.P.	3.9	−0.10	68.88	−0.21	19,507	55.7	0.0	69.3	151.7	66.3	2.0
HEK01-10	Rhyolite	6600 B.P.	4.6	−0.13	71.89	−0.14	23,143	63.3	25.1	90.5	194.4	79.7	1.8
HEK03-10	Rhyolite	4000 B.P.	4.6	−0.18	72.07	−0.17	23,147	64.4	24.2	75.6	165.3	79.9	2.0
<i>Other Icelandic</i>													
BUR20-09	Basalt	~1700 A.D.	0.3	−0.07	49.05	−0.31	1189	2.9	39.3	5.4	14.3	8.6	0.3
RHY01-09	Dacite	Postglacial	6.0	−0.06	68.53	−0.2	35,059	111.0	6.0	83.3	173.1	103.0	3.9
<i>USGS standards</i>													
BHVO-2	Basalt		3.5	0.01									
GSP-2	Granodiorite		2.1	−0.17									

Molybdenum, tantalum and REEs concentrations, and Mo isotopic compositions of all samples, and USGS standards were determined by this study. More REEs data are available in [Electronic annex](#). Mo isotope composition ( $\delta^{98}\text{Mo}$ ) is relative to NIST SRM3134. A minimum of two full procedural duplicate was made for  $\delta^{98}\text{Mo}$  of each sample analysed, and reproducibility (2 s.d.) of all samples is equal or better than  $\pm 0.06\text{‰}$ . Other elemental and isotopic data are taken from [Savage et al. \(2011\)](#).

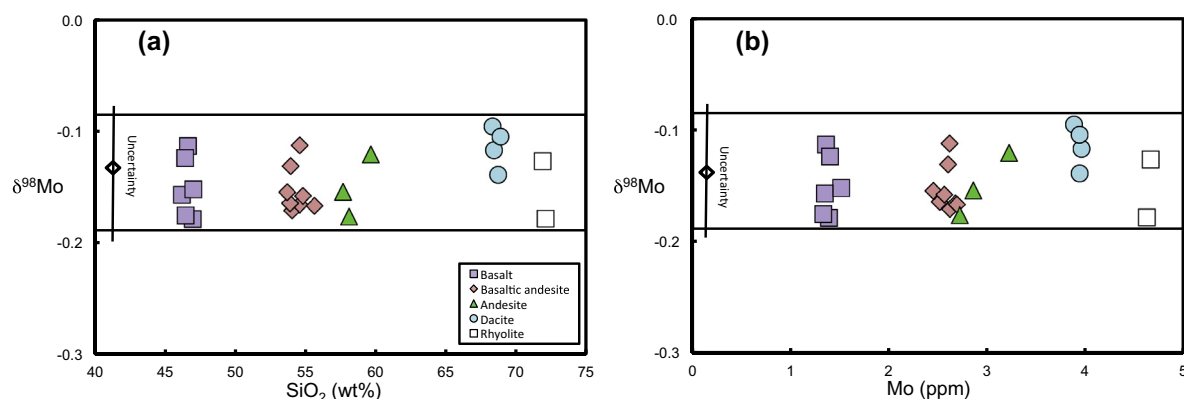


Fig. 1.  $\delta^{98}\text{Mo}$  vs. (a)  $\text{SiO}_2$  content and (b) Mo concentration for Hekla series. Analytical uncertainty is  $\pm 0.06$  (2 s.d.) defined by the long-term reproducibility of USGS standards, BHVO-2 and GSP-2. Each plotted  $\delta^{98}\text{Mo}$  value represents the average of two to four full procedural duplicates and the reproducibilities of all samples are better than  $\pm 0.06$  (2 s.d.). Black parallel lines indicate the 2 s.d. of all samples.

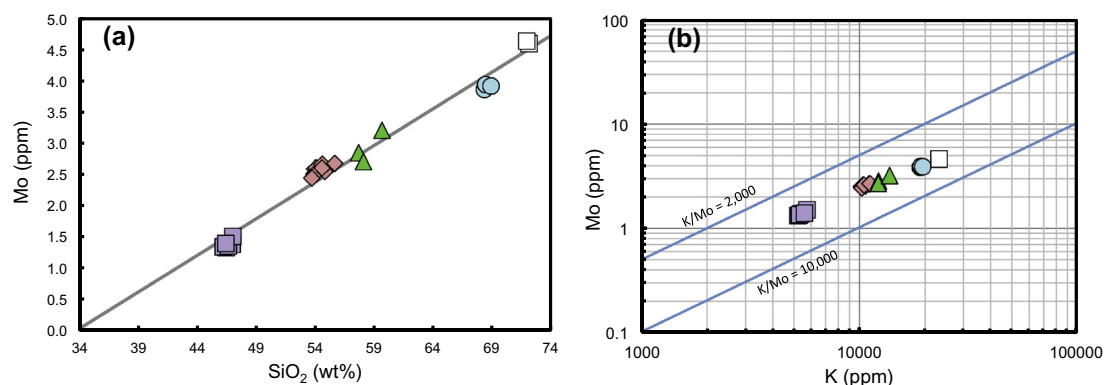


Fig. 2. Mo concentration vs. (a)  $\text{SiO}_2$  and (b) K content, demonstrating the incompatible behaviour of Mo during magmatic fractionation. Symbols as for Fig. 1.

## 5.2. Absence of Mo isotopic contamination by fluid altered materials at Hekla

Notable Mo enrichment and isotope fractionation may easily occur via low-T and hydrothermal processes (e.g. McManus et al., 2002; Siebert et al., 2003, 2006; Hannah et al., 2007; Mathur et al., 2010). Euxinic and oxic marine sediments and Mo-bearing hydrothermal deposits are enriched in Mo, with concentrations significantly higher than in igneous rocks. Moreover, the Mo isotope fractionation associated with sedimentary and hydrothermal processes is usually quite significant. For instance, oxic marine sediments (ferromanganese crusts) throughout Cenozoic and recent times are accompanied by light Mo isotopic compositions ( $\delta^{98}\text{Mo} \sim -1.0\text{‰}$ ; Siebert et al., 2003), whereas modern seawater, as well as paleo-ocean over the last 60 Ma, are characterised by heavy Mo isotopic signatures ( $\delta^{98}\text{Mo} \sim 2.0\text{‰}$ ; Siebert et al., 2003). Hydrothermal ore deposits are also accompanied by large variations in  $\delta^{98}\text{Mo}$  with ranges of, for example,  $1.9\text{‰}$  (Hannah et al., 2007),  $\Delta\delta^{98}\text{Mo} = 2.4\text{‰}$  (Mathur et al., 2010) and  $1.4\text{‰}$  (Greber et al., 2011). Riverine systems on Iceland have been studied for Mo isotopes in two regions, with a variation of  $\delta^{98}\text{Mo}$  from  $-0.5\text{‰}$  to  $1.3\text{‰}$  (Pearce et al., 2010). Therefore, interaction with fluids or materials affected by

low-T or hydrothermal processes should affect the magma in both Mo concentration and isotopic composition.

If the Hekla lavas contained Mo that had been fractionated by low-T processes, the silicic magmas would be particularly affected, as Hekla dacites are thought to have assimilated, or been derived from partial melting of, hydrated Icelandic crust (Sigmarsson et al., 1992; Chekol et al., 2011). The dacites, like basalts to andesites, show no hint of anomalous Mo isotopic compositions or concentrations (Figs. 1 and 2). A study of a low-T ocean ridge flank hydrothermal system showed that geothermal springs are enriched in Mo content with lighter Mo isotopes than bottom waters (McManus et al., 2002; Wheat et al., 2002), indicating release of Mo from oceanic basalt into fluid during seawater/rock interaction. Therefore, hydrothermally altered oceanic basalt should be somewhat depleted in Mo with high La/Mo, and the interaction with seawater may lead to a heavier Mo isotope composition. In this regard, Hekla dacites, as putative melts of this altered crust, might be expected to have higher La/Mo and to be isotopically heavier than Hekla basalts and basaltic andesites. However, given that the entire compositional range of Hekla samples including the dacites follow a single magmatic differentiation trend (Fig. 2), possess remarkably uniform Mo isotope composition (Fig. 1) and if anything have

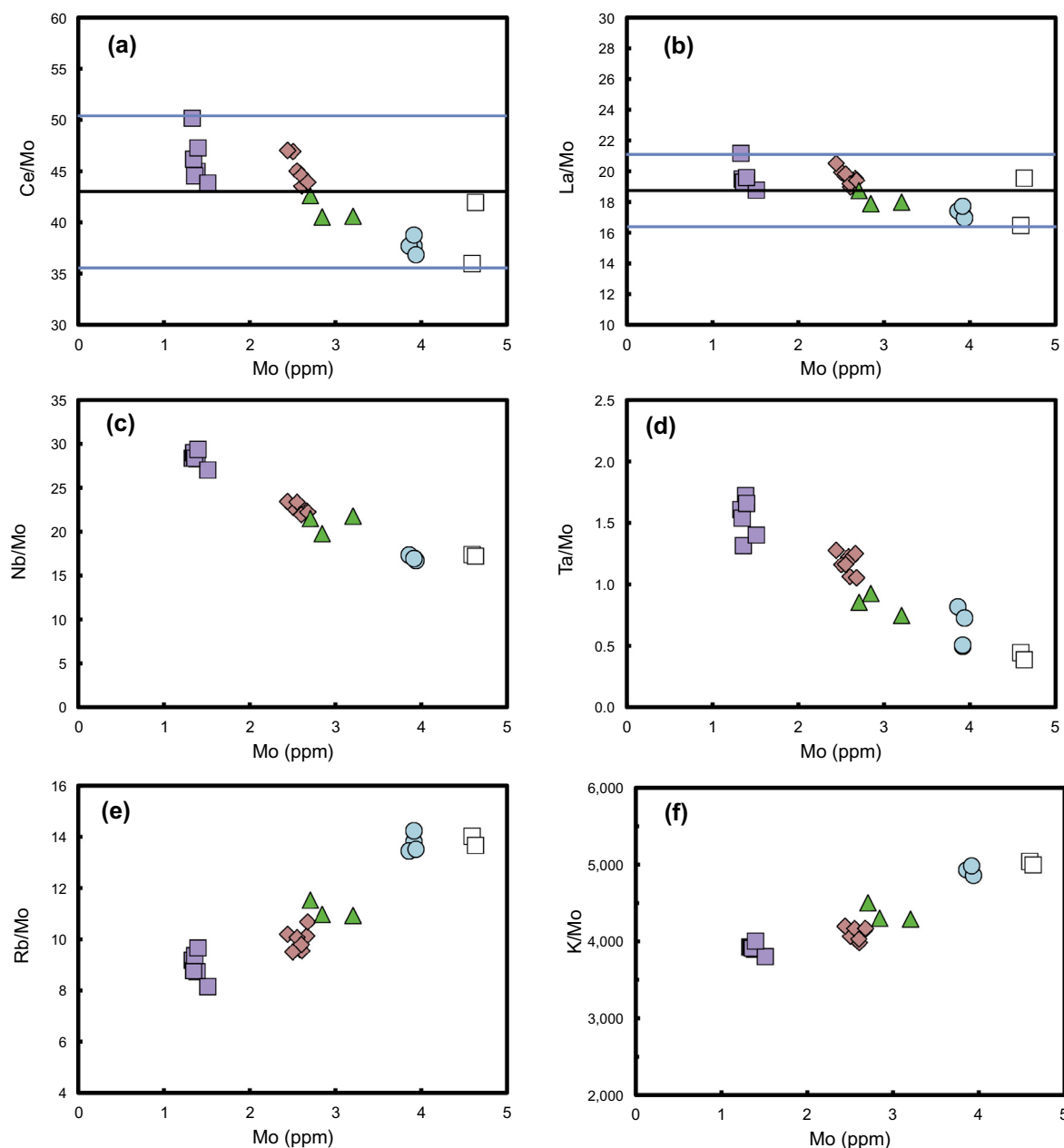


Fig. 3. Mo concentration vs. (a) Ce/Mo, (b) La/Mo, (c) Nb/Mo, (d) Ta/Mo, (e) Rb/Mo and (f) K/Mo. Plots (a) and (b) black lines: mean; grey lines: 2 s.d. of all samples, showing the amount of dispersion of the trace element ratios. Plots (c), (d), (e) and (f) indicate that Mo is more incompatible than Nb and Ta, but less so than Rb and K. Symbols as for Fig. 1. See text for discussion.

a slightly low La/Mo (Fig. 3) we conclude that there is no evidence of non-magmatic components affecting the magmas or their sources. This is reinforced by similar O isotope signatures in Hekla magmas of basaltic to silicic composition (Sigmarsson et al., 1992), showing no indication of effects from low-T or hydrothermal alteration.

### 5.3. Why has there been no molybdenum isotope fractionation at Hekla?

Large Mo isotope variations have been observed in high-T to low-T molybdenite deposits (Hannah et al.,

2007; Mathur et al., 2010; Greber et al., 2011), suggesting that formation of Mo-sulphide is very likely to cause significant Mo isotope fractionation. Also sulphides crystallised in basaltic magma appear to have distinctly heavy Mo isotope compositions relative to their host rocks/magmas (Voegelin et al., 2012). Therefore, removal of small quantities of immiscible sulphide liquids or crystallisation of Mo-bearing sulphides would be expected to cause a notable Mo isotopic fractionation. Hekla lavas show a pronounced drop in sulphur concentration through two orders of magnitude from basalt to andesite and dacite (Fig. 4a). If this compatible behaviour of S is in response to sulphide extraction,

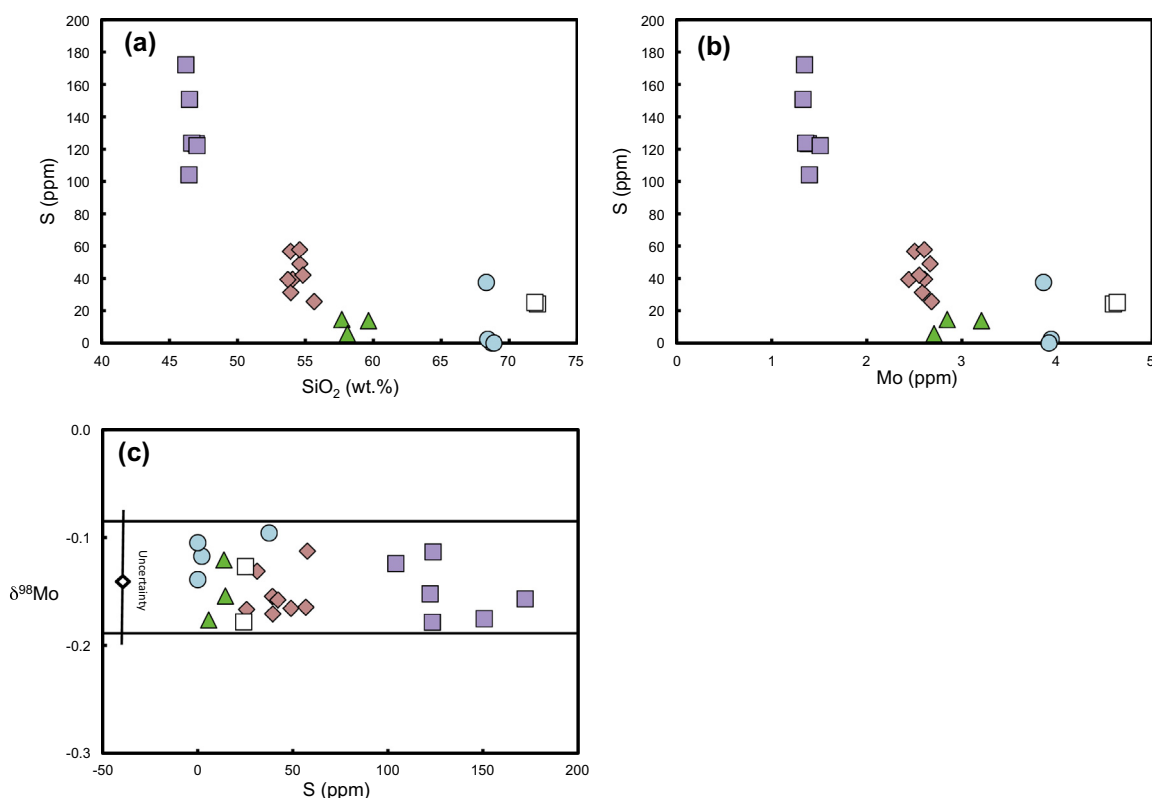


Fig. 4. (a) SiO<sub>2</sub> content vs. S concentration, (b) Mo concentration vs. S concentration and (c)  $\delta^{98}\text{Mo}$  vs. S concentration. Symbols and lines as for Fig. 1.

one might expect detectable systematic evolution of Mo isotope composition as the magma differentiates.

Melt inclusion and experimental studies provide evidence that the differentiation of Hekla magmas might have started with S-undersaturated parental basaltic melts and become S-saturated in more evolved basaltic melts when the K<sub>2</sub>O content reached ~0.6 wt.% (Moune et al., 2009). Hekla basalts analysed in this study are all characterised by K<sub>2</sub>O  $\geq$  0.6 wt.% and may therefore have achieved magmatic sulphide saturation. Although Mo in the form of Mo(VI) may be present through a wide range of oxygen fugacity (i.e. from air to IW+4) in silicate melts predominantly as molybdate species ( $\text{MoO}_4^{2-}$ ) (Candela and Holland, 1984; Holzheid et al., 1994; Farges et al., 2006a), it can also form sulphidic complex (Mo-S) in silicate melt at moderate sulphur and oxygen fugacity (Farges et al., 2006b), which facilitates the formation of molybdenite or Mo being accommodated in sulphide (e.g. pyrite), given the low oxygen fugacity near FMQ (Baldridge et al., 1973; Portnyagin et al., 2012) and S-saturated conditions in Hekla basaltic magmas. This would in part explain the dramatic drop in S concentration (Fig. 4a) with the formation of sulphide. However, the expected loss of Mo and fractionation of Mo isotopes due to sulphide extraction are not observed (Fig. 4b and c). Alternatively, the removal of sulphur from the Hekla system could also have resulted from sulphur degassing (Moune et al., 2007). This process would have not had a detectable impact on the Mo concentration or isotope

composition in Hekla lavas given the observed isotopic uniformity and incompatible behaviour of Mo. Hence, the lack of both Mo isotope fractionation and a positive correlation between Mo and S in the Hekla series demonstrates that Mo does not partition into sulphide and is not removed from the melt or isotopically fractionated. This provides powerful evidence that sulphur content is not always of significance for the behaviour of Mo and its isotopic composition in magmatic systems. This agrees with an experimental work showing that Mo is only weakly influenced by fractionation of sulphides (Lodders and Palme, 1991).

In addition to chalcophile tendency to form sulphides, small amounts of Mo may be incorporated into silicate and oxide minerals, such as olivine, pyroxene, magnetite and ilmenite (Audétat, 2010; Wager and Mitchell, 1951). Audétat (2010) reports the Mo concentrations in olivine (<0.1  $\mu\text{g/g}$ ), plagioclase (<0.2  $\mu\text{g/g}$ ), magnetite (2  $\mu\text{g/g}$ ), apatite (<0.5  $\mu\text{g/g}$ ) and ilmenite (9  $\mu\text{g/g}$ ), determined by LA-ICP-MS in a porphyry deposit. It therefore appears that Mo partitions more into oxide than silicate. However, Voegelin et al. (2014) found that Mo can be incorporated in silicate minerals, such as clinopyroxene, olivine and orthopyroxene, and is particularly enriched in hornblende and biotite, both of which have a distinctly light Mo isotope composition relative to the bulk rock. These authors thus propose that crystallisation of amphibole and biotite may alter the Mo isotope composition of magma and suggest minimum Mo isotope fractionation factors between silicate melt and coexisting minerals of



$\Delta^{98}\text{Mo}_{\text{hbl-melt}} \geq 0.5\text{‰}$  and  $\Delta^{98}\text{Mo}_{\text{bio-melt}} \geq 0.3\text{‰}$  for hornblende and biotite respectively. Hence, a fraction of  $\sim 15\%$  amphibole or  $\sim 25\%$  biotite must be separated from the system to shift the bulk isotopic composition to a detectable level ( $0.06\text{‰}$ ). The evolution of Hekla magmas has been documented to involve crystallisation and separation of olivine, titaniferous magnetite, and plagioclase (Balldridge et al., 1973). Petrographic examination of a selection of the Hekla samples in this study, shows that olivine, clinopyroxene and plagioclase feldspar are the major crystallising phases, along with accessory apatite, magnetite and minor zircon (Savage et al., 2011). There is no evidence of fractionation of amphibole and/or biotite in Hekla magmas. Although olivine, clinopyroxene and magnetite have been observed to accommodate Mo, the uniformity of Hekla lavas in Mo isotopic composition suggests that isotopic fractionation due to the uptake of Mo into these minerals is insignificant. Molybdenum isotopes in a magmatic suite may therefore be utilised to identify amphibole and biotite fractionation in magmatic systems free of disturbances by other processes.

In summary, in spite of the potential complexities of magmatic systems, the Mo isotope system in Hekla appears to be rather insensitive to fractionation of the documented phases, i.e. olivine, pyroxene, plagioclase and accessory minerals. Although the data cannot preclude fractionation during differentiation in other geological settings, for instance, where a significant proportion of amphibole and biotite crystallise during magmatic differentiation, they are a good indication that resolvable fractionation in Mo isotopes is unlikely to occur even with major sulphur removal.

#### 5.4. Molybdenum isotopes and fluid exsolution in silicic magma systems

High  $\text{H}_2\text{O}$  contents (6.5 wt.%) were found in melt inclusions of fayalitic olivines from silicic Hekla melts (Portnyagin et al., 2012), which provides support for the possibility of fluid exsolution from the melts. Given that Mo partitions strongly into fluid (Zajacz et al., 2008; Audétat, 2010), fluid exsolution should therefore produce a drop in Mo concentration in silicic melts and potentially be accompanied by isotopic fractionation.

However, recent work on Li isotopes provides supporting evidence against fluid-related isotopic effects at Hekla (Schuessler et al., 2009). Lithium is a moderately incompatible and fluid-mobile element which strongly partitions into aqueous fluids relative to co-existing silicate melt (Webster et al., 1989). Fluid exsolution should thus cause a decrease in Li concentration during magmatic differentiation at Hekla. However, like Mo, the Li content also shows a positive linear relationship with magmatic differentiation indicators (e.g.  $\text{SiO}_2$ ,  $\text{K}_2\text{O}$ ), demonstrating the incompatible behaviour of Li in magmatic systems (Schuessler et al., 2009). Several studies have shown that significant Li isotope fractionation occurs as a result of fluid exsolution from melts (Teng et al., 2006; Wunder et al., 2006), indicating the vulnerability of Li isotopes to fluid/melt interaction in magmatic systems. Consequently, fluid exsolution from Hekla melts can be inferred to have been minor based on

the constant Li isotopic composition observed in Hekla lavas (Schuessler et al., 2009).

Similar arguments can also be made by Mo, which has been observed to partition strongly into magmatic fluids in granitic systems, with high fluid/melt partition coefficient ranging from 10 to 20 (Zajacz et al., 2008; Audétat, 2010), significantly higher than those determined experimentally, which are typically lower than 5.5 (Candela and Holland, 1984; Keppler and Wyllie, 1991). Molybdenites precipitated from fluids in granitic systems display a large variation of Mo isotope composition (Hannah et al., 2007; Mathur et al., 2010; Greber et al., 2011, 2014). The early mineralisation of molybdenite from magmatic-hydrothermal fluids is found to be much heavier than the residual rhyolitic magma, indicating that fluid exsolution process enriches the fluid in heavier isotopes relative to coexisting melts (Greber et al., 2014). Such an effect cannot be seen in our silicic samples as dacites and rhyolites follow the overall magmatic differentiation trend (Fig. 2). The constant Mo isotope composition for silicic samples is inconsistent with significant fluid exsolution unless for some reason it did not transport Li or Mo. Given the fluid-mobile behaviour of Mo and robustness of the Mo isotope system during fractional crystallisation, Mo, like Li, may be a valuable tracer of melt/fluid interaction.

## 6. CONCLUSIONS

Lavas from Hekla demonstrate no resolvable Mo isotope fractionation, with an average composition of  $\delta^{98}\text{Mo} = -0.15 \pm 0.05\text{‰}$  (2 s.d.). Molybdenum behaves as an incompatible element with a bulk D similar to La during magmatic differentiation. Both the Mo concentration and isotope composition are insensitive to sulphur or sulphide content in Hekla magmas. The absence of Mo isotope fractionation during magmatic differentiation at Hekla suggests that Mo can potentially be used as an indicator of parental magma composition in anhydrous systems and a potential discriminant of assimilation processes. Given that Mo partitions into fluid readily during magmatic fluid exsolution, potentially accompanied with Mo isotope fractionation, it could also be an effective tracer for magmatic fluids in hydrothermal systems.

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## APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2015.04.011>.

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